

Inner-Shell Photoelectron Spectrum of PF_3 and CO_2

N. Berrah¹, K.J. Børve², J. Bozek³, T. X. Carroll⁴, J. Hahne⁵, E. Kuk^{1,3}, L. J. Sæthre², and T. D. Thomas⁵

¹Physics Department, Western Michigan University, Kalamazoo, MI 49008

²Department of Chemistry, University of Bergen, N-5007 Bergen, Norway.

³Advanced Light Source, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720

⁴Keuka College, Keuka Park, NY 14478

⁵Oregon State University, Corvallis, OR 97331-4003

INTRODUCTION

High-resolution inner-shell photoelectron spectra of molecules reveal a number of features that relate to the chemistry of the molecule and to the chemical physics and dynamics of the ionization process. Among these are chemical shifts of the ionization energy due to the local environment of the core-ionized atom, vibrational excitation that occurs during ionization, line broadening that results from the finite lifetime of the core-ionized state, distortion of the line shape that results from interaction of the outgoing photoelectron with the Auger electron (emitted in the deexcitation of the core hole), localization-delocalization effects that can occur in molecules with equivalent atoms (such as HCCH), and, for ionization of levels with $l > 0$, molecular-field splitting, which removes the degeneracy of levels such as $2p_{3/2}$ that are degenerate in the spherical case.

During 1999 our efforts were focused on analyzing the inner-shell molecular photoelectron spectra taken during our runs in 1998 and 1997. Results on CH_4 (discussed in our 1998 report), which illustrate the effects of lifetime and interaction with the Auger electron on the line shape as well as the vibrational structure, were published during 1999. [1] Work on the carbon 1s photoelectron spectrum of CO_2 , discussed below, shows that the lifetime of the carbon 1s hole in this molecule is significantly shorter than expected from simple models, while that on the phosphorous 2p photoelectron spectrum of PF_3 , also discussed below, shows the importance (and difficulty) of understanding the effect of molecular-field splitting on the spectrum. Both spectra show the effect of vibrational excitation and provide information on the changes in molecular geometry that accompany core-ionization.

CARBON 1s CORE-HOLE LIFETIME IN CO_2 [2]

An ion with a missing core electron is in a highly excited state and decays rapidly via Auger decay. For a carbon 1s hole, this involves valence electrons, one to fill the core hole and one that is ejected, carrying away the excess energy. The rate for this process depends on the density of valence electrons at the atom with the core hole and is expected to depend critically on factors that affect this density. Specifically, it is predicted that the lifetime for deexcitation of a core hole in CH_4 will be less than that in CO_2 , since the electronegative oxygen withdraws electron density from the carbon atom in CO_2 . [3,4] The lifetimes, τ , are reflected in the linewidths, Γ , of the spectral lines by the relationship $\Gamma \tau = \hbar$; for carbon 1s, typical lifetimes are around 5 fs, corresponding to linewidths of about 100 meV. For CH_4 , the linewidth is predicted to be 96 meV [3], and this is in good agreement with our previously reported value of 95 meV. [1] For CO_2 the linewidth is predicted to be 66 meV, in keeping with the idea that valence electrons are withdrawn from the core-ionized carbon by the electronegative oxygen. The measured linewidth is, however, 99 meV, considerably greater than

predicted and essentially indistinguishable from that found for CH_4 .

The theoretical calculations are based on a one-center model, which assumes that only those electrons that are localized on the atom with the core hole can participate in Auger deexcitation of the core hole. This model has been the basis for most theoretical calculations of molecular Auger decay. Our results suggest, however, that the valence electrons on the oxygen atoms may play a role in the Auger decay of the carbon 1s core hole in CO_2 , and, hence, that a multicenter model may be necessary to describe the Auger process.

MOLECULAR-FIELD SPLITTING AND VIBRATIONAL STRUCTURE IN THE PHOSPHORUS 2p PHOTOELECTRON SPECTRUM OF PF_3 [5]

In simplest approximation, the three 2p orbitals of an atom are degenerate. If spin-orbit coupling is important, then this degeneracy is removed, and we have $2p_{1/2}$ and $2p_{3/2}$ orbitals for a spherical atom. In a molecular environment it is possible that the molecular field further splits the degeneracy of the $2p_{3/2}$ orbital into two components corresponding approximately to $\pm 1/2$ and $\pm 3/2$ projections of the angular momentum on the molecular symmetry axis. In addition, for a molecule, there is likely to be vibrational excitation accompanying core ionization, since the equilibrium bond lengths for the core-ionized molecule are usually different from those for the neutral molecule. Both of these features are apparent in the phosphorus 2p photoelectron spectrum of PF_3 , illustrated in Fig. 1. In this figure, the points show the experimental data and the solid line through the points shows a least-squares fit to the data. The unshaded structure to the right shows the fit to the vibrational structure of the $2p_{1/2}$ group. The two shaded structures, which are identical in shape to the $2p_{1/2}$ structure show the fits to the $2p_{3/2, \pm 1/2}$ and $2p_{3/2, \pm 3/2}$ groups. The adjustable parameters in the fit are the positions of the peaks in the $2p_{1/2}$ group, the spin-orbit splitting between the $2p_{1/2}$ group and the centroid of the $2p_{3/2}$ group (881 meV), and the molecular-field splitting between the two components of the $2p_{3/2}$ groups (146 meV).

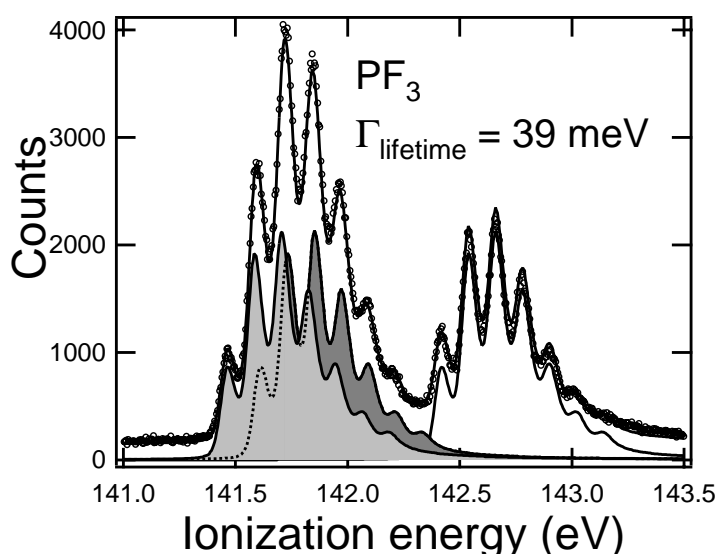


Figure 1. Phosphorus 2p photoelectron spectrum of PF_3

The pronounced vibrational structure seen in the phosphorus 2p core-ionization of PF_3 indicates that there is a significant bond-length change accompanying ionization. From the measured Franck-Condon factors together with a model that includes the measured anharmonicity, we can infer that the PF bond contracts by 6.0 pm. A simple theoretical model based on the equivalent-cores approximation, which has proven successful for the analysis of vibrational structure in the core ionization

of carbon 1s electrons in hydrocarbons [6], predicts a bond contraction of only 4.2 pm, and, therefore, predicts too little vibrational excitation. Modifying this model with a different basis set produces excellent agreement with experiment, but, at this stage, it is impossible to say whether or not this will be a generally useful approach for understanding the vibrational structure seen in the 2p ionization of second-row atoms. An *ab initio* hole-state calculation that has worked quite well for methane [1] gives a predicted bond-length change that is close to the experimental value, but low by 0.8 pm.

The molecular-field splitting of the $2p_{3/2}$ line in the spectrum, 146 meV, is significant. A simple point-charge, crystal field, model, which would predict a very small splitting, is not adequate to describe this phenomenon. It is necessary to consider the effect of the polarization of the valence electrons because of bonding, and, more important, it is necessary to take account of core-valence correlation in understanding this splitting. [7] When these effects are included, we obtain a predicted value for the molecular-field splitting of 136 meV, in good agreement with the experimental value.

REFERENCES

1. T. X. Carroll, N. Berrah, J. Bozek, J. Hahne, E. Kukk, L. J. Sæthre, and T. D. Thomas, Phys. Rev. A, **59**, 3386 (1999).
2. T. X. Carroll, J. Hahne, T. D. Thomas, L. J. Sæthre, N. Berrah, J. Bozek, and E. Kukk, Phys. Rev. A. in press (2000).
3. M. Coville and T. D. Thomas, Phys. Rev. A **43**, 6053 (1991).
4. F. P. Larkins, Aust. J. Phys. **49**, 457 (1996).
5. K. J. Børve, L. J. Sæthre, J. D. Bozek, J. True, and T. D. Thomas, J. Chem. Phys. **111**, 4472 (1999).
6. T. D. Thomas, L. J. Sæthre, S. L. Sorensen, and S. Svensson, J. Chem. Phys. **109**, 1041 (1998).
7. K. J. Børve and T. D. Thomas, J. Chem. Phys. **111**, 4478 (1999).

This work was supported by the National Science Foundation under Grant No. CHE-9727471, by the Divisions of Chemical and Material Sciences, Office of Energy Research, of the U. S. Department of Energy, and by the Research Council of Norway (NFR).

Principal investigator: T. Darrah Thomas, Department of Chemistry, Oregon State University.
Email: thomast@chem.orst.edu. Telephone: 541-737-6711.